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THE ODTX SYSTEM FOR THERMAL IGNITION AND THERMAL SAFETY STUDY OF ENERGETIC MATERIALS

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Understanding the response of energetic material to thermal event is very important for the storage and handling of energetic materials. The One Dimensional Time to Explosion (ODTX) system at the Lawrence Livermore National Laboratory (LLNL) can precisely measure times to explosion and minimum ignition temperatures of energetic materials at elevated temperatures. These measurements provide insight into the relative ease of thermal ignition and allow for the determination of kinetic parameters. The ODTX system can potentially be a good tool to measure violence of the thermal ignition by monitoring the size of anvil cavity. Recent ODTX experimental data on various energetic materials (solid and liquids) are reported in this paper.

INTRODUCTION

Measurements of time to thermal ignition/explosion at elevated temperature is of great interest for the study of explosive handling safety and thermal decomposition kinetics. The One Dimensional Time to Explosion (ODTX) system has been used for over 3 decades at LLNL and other laboratories as a tool to study thermal ignition behaviors of energetic materials [1,2,3,4].

The ODTX testing generates two important technical data points for energetic materials mixtures[5]:
    (1) Lowest temperature at which thermal ignition would occur (T_{li}) and
    (2) Times to thermal explosion at temperatures above T_{li} for the calculation of activation energy and frequency factor.

Note: This measurement only pertains to 1.27-cm diameter spherical parts and larger parts will react at a lower temperature although longer thermal soaks would be required to heat up the larger mass.

(1) Threshold temperature for thermal ignition
Knowing the lowest thermal ignition temperature (T_{li}) for each energetic material is very important for safe storage and transportation to avoid incidental detonation. Two possible scenarios for causing incidental thermal explosions are described below:

1. Energetic materials may be kept and stored in closed containers that are exposed to hot climates. During the summer in some desert areas, the outdoor temperature may exceed 120°F while the surface temperature of metallic storage containers exposed to the sun may exceed 170°F (77°C). Given enough time, some liquid-based formulations may ignite and explode.
2. If containers storing energetic materials are kept inside a parked van or truck with windows closed for an extended period of time, the air inside the van may exceed 170°F in the summer. Given enough time, some liquid-based formulations in the containers may ignite and explode.

For larger quantities of energetic materials (assuming similar shape), thermal runaway would occur at even lower temperatures than those that caused runaway of the 1.27-cm diameter spherical samples tested. The hazard is even worse than stated, although longer thermal soaks would be required to bring a large mass of material to thermal ignition temperature.

(2) Time to Explosion Data, Activation Energy, and Frequency Factor
Times to thermal explosion at temperatures above T_{li} for the calculation of activation energy and frequency factor as well as the decomposition kinetics parameters are represented by a single-

step Prout-Tompkins (Arrhenius) model shown below.

$$\frac{dx}{dt} = -A \exp\left(-\frac{E}{RT}\right) x^n (1 - qx)^m \quad (1)$$

Where

x = mass fraction of reactant remaining

A = frequency factor; E = the activation energy; R = universal gas constant

T = temperature; n, m, q = Prout-Tompkins model kinetics parameters.

Explosion or deflagration is an ultra-fast chemical reaction that releases a tremendous amount of energy in a very short time (microseconds to milliseconds). The activation energy (E), the frequency factor (A), and Prout-Tompkins model kinetics parameters for the temperature-dependent reaction can be calculated from the ODTX data. They are useful data for simulation and modeling in the ALE3D (Arbitrary Lagrangian-Eulerian in Three Dimensions) computer code. The Arbitrary Lagrangian-Eulerian in Three Dimensions (ALE3D) computer code has been used in many applications to predict both the timing and violence of thermal ignition events [2].

SYSTEM DESCRIPTION

The ODTX system is shown in Figure 1 with main components labeled. The experiment involves heating a 1.27-cm diameter spherical sample in a 1.27-cm diameter spherical cavity between two aluminum anvils. The sample is remotely delivered to the anvil cavity via the sample delivery system. A cross-sectional view of the anvil cavity is shown in Figure 2. The hydraulic piston drives the top heater and anvil downward toward the bottom heater and anvil. A copper O-ring provides an excellent seal with no gas leakage when the two knife-edges on the aluminum anvils compress it. Two band heaters are used for heating top and bottom anvils to a predetermined temperature. A microphone sensor measures a sound signal, which indicates the time at which a thermal ignition occurs.
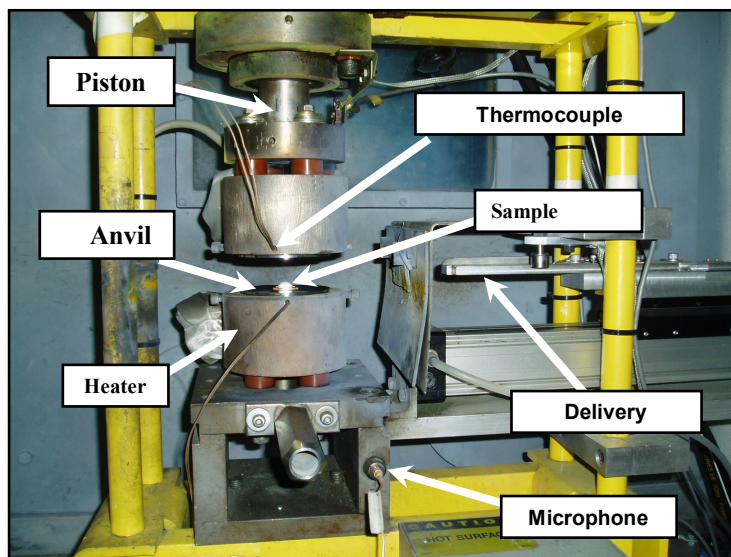

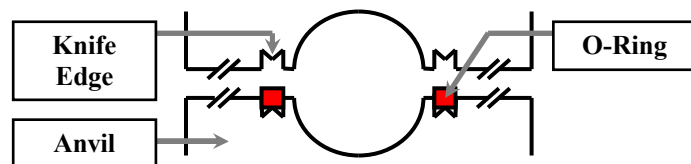**Figure 1. ODTX apparatus with key components labeled.**

Figure 2. Conceptual cross section of 1.27-cm diameter spherical anvil cavity.

Energetic materials in any sample configurations can be tested in the ODTX system. An aluminum shells is used to hold powder samples, pasty samples, or liquid samples. The shell is assembled and formed a sphere with two hemispheres and a center ring. One of hemispheres has a pinhole on the top for loading liquid or powder samples, as shown in Figure 3. Pressed and cast samples are delivered to the cavity of aluminum anvils directly without the use of aluminum shell. Figure 4 show a typical ODTX pressed sphere.

Figure 3. Aluminum shell for testing liquid, powder, or pasty samples.

Figure 4. Partial view of spherical TATB sample (1.26-cm diameter).

RECENT EXPERIMENTAL RESULTS

Times to thermal explosion for TATB-related formulations

TATB is less sensitive to thermal ignition than most conventional high explosives such as HMX, RDX, and PETN. At temperature below 230 C, a 1.26-cm spherical pressed part would not thermally explode. Several TATB materials were recently tested in the ODTX system and the material information and times to explosion data are shown in Table 1 and Figure 5, respectively. The ODTX data for HMX, RDX, and PETN are also shown in the figure for comparison.

Prior to 2000, ODTX experiments were performed in an older version of ODTX system that used older electronics and did not have the remote sample delivery function. Figure 5 shows a more consistent ODTX data for the wet aminated TATB obtained from the current ODTX system than

those obtained in 1981 from the old ODTX system. The ultrafine TATB, with a mean particle size less than 5 μm, exploded at slightly shorter times than the wet aminated TATB (mean particle size 52 μm) did at the same temperature. The greater surface area of the finer TATB particles allowed gaseous reaction products to be produced faster than coarser TATB particles when thermal decomposition process started. HMX also exhibited same behavior as TATB as shown in Figure 6 [6].

TABLE 1. TATB sample information

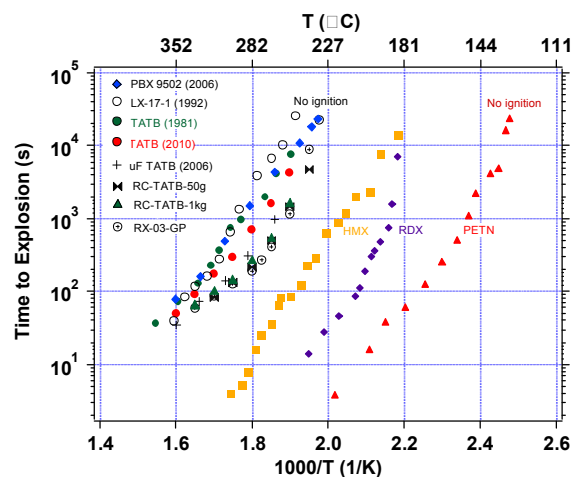| Samples	Material information	Mean particle size, μm	Test date
LX-17-1	92.5% TATB, 7.5% Kel-F 800	N/A	1992
PBX 9502	95.0% TATB, 5.0% Kel-F 800	N/A	2006
TATB	Wet-aminated	N/A	1981
TATB	Wet aminated	52	2010
uF TATB	Fine TATB powder	≤ 5	2006
RC-TATB	Re-crystallized TATB, 50-g batch	18	2010
RC-TATB	Re-crystallized TATB, 1.0-kg batch	43	2010
RX-03-GP	92.5% Re-crystallized TATB, 7.5% Kel-F 800	N/A	2009

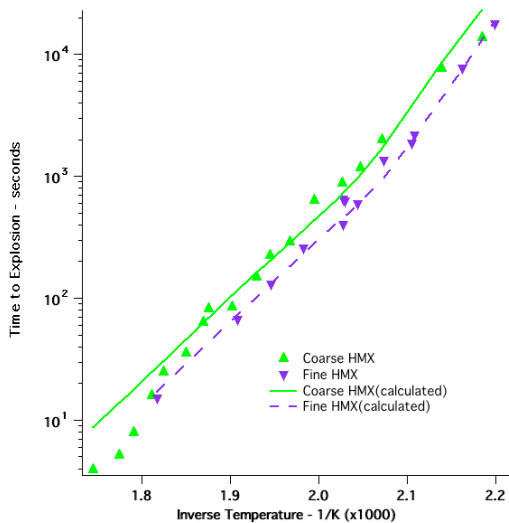**Figure 5. ODTX results of several TATB-related samples.**

Figure 6. ODTX results of fine and coarse HMX [6].

Figure 7. ODTX results of several AP-related formulations (PS-4, PS-RMU, and HPP).

Times to thermal explosion for AP-related formulations

Ammonium perchlorate (AP) is a key ingredient in many commercial and military propellants. AP, aluminum, and binder can be casted into forms for various applications. Several AP-related formulations were tested in the ODTX system in the 1990s and times to explosion data are shown in Figure 7. Also shown is the data for a high performance propellant material (HPP) which we did the testing in 2009. Figure 7 shows the AP/Al formulations are more sensitive to thermal ignition than TATB but less sensitive to TNT, HMX, RDX and PETN. Remarkable similarity of thermal sensitivity between PS-4 and HPP was observed. PS-RMU is slightly less sensitive to thermal ignition than PS-4 and HPP. Some HPP data deviated significantly from the curve. This was due to the surface imperfection of the cast HPP spheres (data point 1). The presence of pinholes and pores on the surface made the sample more sensitive than other spheres (data points 2 and 3) due to higher porosity and greater surface area for heat transfer and gas production.
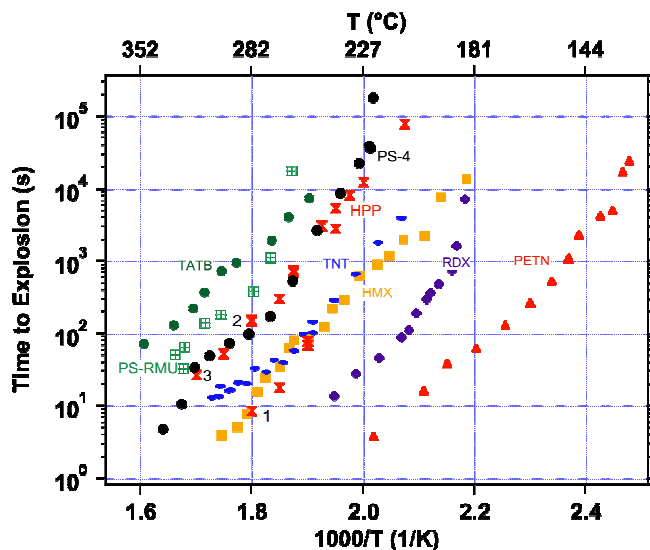
Times to thermal explosion for pasty formulations

Three pasty formulations (Table 2) were tested in the ODTX system with the results shown in Figure 8. The more sensitive ingredient in the formulation dominates the thermal sensitivity. Figure 8 shows the ODTX data for C-4 are similar to those of RDX . The thermal sensitivities of Semtex 1A and Semtex 1H are very similar to that of PETN.

TABLE 2. Pasty materials tested in the ODTX system

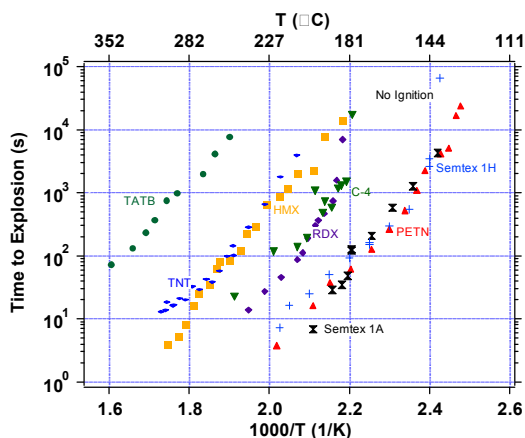| Samples	Material information	Test date
C-4	RDX and Semtex oil	2002
Semtex 1A	PETN, Semtex oil, and binder	2006
Semtex 1H	RDX, PETN, Semtex oil, and binder	2009

Figure 8. ODTX results of three pasty formulations.

Times to thermal explosion for energetic liquid mixtures

Liquid oxidizers, when mix with fuels, form energetic liquids. Several energetic liquid mixtures were recently formulated and tested in the ODTX system with the results shown in Figure 9. In general, the liquid mixtures we have tested so far were more sensitive to thermal ignition than PETN. The error bars of ODTX data for liquid explosives scattered more than those of solid explosives. This is typical of liquid explosives in that they have high vapor pressures and more volatile.
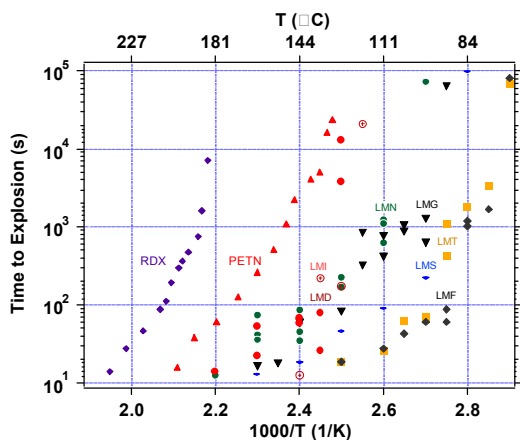

Figure 9. ODTX results of several liquid explosives.

DENT ANALYSIS FOR RELATIVED DEGREE OF THERMAL IGNITION VIOLENECE

After the ODTX testing, each anvil was scanned with a surface profilometer for dent analysis. Figure 10 shows anvils before and after the testing. Volumes of the resulting craters in the aluminum anvils were measured to obtain a relative degree of violence of the explosions. The most violent reactions, defined as those that form the largest craters, occur in the middle of thermal explosion temperature range, at which the heat transfer reaches the center of sphere, and thermal runaway occurs there first and then proceeds through the entire charge of material. At the highest temperatures, only the outer edges of the explosive are heated to rapid reaction and the center of the sphere does not react before the anvils separate. At the lowest temperatures, the entire explosive sphere is producing gaseous products before the thermal runaway. This cavity volume increase pattern is only applied to pressed parts of high density.

Crater volume increases for several materials are listed in Table 3 and Figure 11. LX-04 (85% HMX, 15% binder), with a volume increase of 1.52 cc per gram of sample tested, was the most violent. TATB showed the least thermal ignition violence. Table 3 also the relative degree of thermal ignition violence, using LX-04 for comparison.

In general, the thermal ignition violence is much lower that the detonation violence due to differences in pressure, temperature and degree of reaction. The thermal ignition only generates about 1.0 kbar pressure[4], much lower than that from detonation. Modeling and experimentation are being planned to conduct detonation in confined aluminum anvils to determine the crater volume increases for several high explosives. Comparison of thermal ignition violence with detonation violence would become possible when the work starts in the fiscal year 2010-2011.

Figure 11 shows the test temperature and volume

Figure 10. Anvils before and after the ODTX testing of Semtex 1H

TABLE 3. Crater volume increase and relative degree of thermal ignition violence

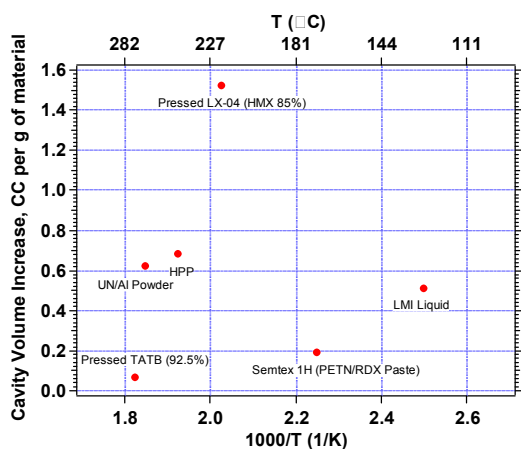| Material	Average volume increase, cc/g	Relative degree of violence
LX-04, pressed	1.52	1
HPP, casted	0.68	0.45
UN/Al, powder	0.62	0.41
LMI, liquid	0.51	0.34
Semtex 1H, paste	0.19	0.13
TATB, pressed	0.07	0.05

Figure 11. Average crater (cavity) volume increases.

CONCLUSIONS

The ODTX system is a useful tool for the measurements of thermal sensitivity and thermal decomposition kinetic parameters. Samples of all configurations (solids, powders, pastes, and liquids) can be tested in the system. TATB related formulations are very insensitive to thermal ignition; below 230 C, they would not ignite and explode. Most of energetic liquids we have tested show higher thermal sensitivity than PETN. Some energetic liquids could ignite at temperatures as low as 80 C. Thus, operational handling and storage of energetic liquid mixtures in hot climates or conditions require careful planning and execution. Measures must be taken for safe storage of these mixtures to avoid incidental thermal ignition. The ODTX testing can also generate useful data for determining relative degree of thermal ignition violence of energetic materials.

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